articles

History of the Mediterranean salinity crisis

Kenneth J. Hsü
Geological Institute, ETH, Zurich, Switzerland

Lucien Montadert
Institut Français du Pétrole, Rueil-Malmaison, France

Daniel Bernoulli
Geologisches Institut, Universität Basel, Basel, Switzerland

Maria Bianca Cita
Istituto di Geologia, Università Milano, Italy

Albert Erickson
Department of Geology, University of Georgia, Athens, Georgia

Robert E. Garrison
Earth Sciences Board, University of California, Santa Cruz, California

Robert B. Kidd
Institute of Oceanographic Sciences, Wormley, UK

Frederic Mèlierès
Laboratoire de Géologie Dynamique, Université de Paris, Paris, France

Carla Müller
Geologisch-Paläontologisches Institut, Johann Wolfgang Goethe Universität, Frankfurt, FRG

Ramil Wright
Department of Geology, Florida State University, Tallahassee, Florida

A history of geodynamic evolution of the Mediterranean leading to the salinity crisis is outlined, based on the 'desiccated deep-basin model'. An accurate portrayal of the crisis is presented, based on data from new drilling and studies of on-land geology.

THE discovery of the Mediterranean Evaporite by the drilling from Glomar Challenger in 1970 proved that salt exists under deep-sea floor[1], and demonstrated that giant salt deposits could have been formed within a relatively short geological time[2]. The almost synchronous onset and termination of the Mediterranean salinity crisis implies catastrophic changes of environments in a region over two and half million square kilometers in extent. This fact did much to throw doubts on Lyell's substantive uniformitarianism[3].

The significance of the Deep Sea Drilling Project (DSDP) discovery was, however, shadowed by controversies. That the Mediterranean Evaporite is Messinian (Late Miocene) in age seemed to be just about the only concensus after the Leg 13 drilling. Even the shipboard scientific staff could not reach an agreement on the genesis of this unusual formation. Chapter 43 of the Leg 13 cruise report presenting the desiccated deep-basin model (ref. 4) was authored by K. J. Hsü, Maria Cita, and W. F. B. Ryan because they were the only members of the shipboard staff totally convinced of its plausibility. Alternative interpretations were given by other shipboard staff in the Initial Cruise Reports and later in other publications[5,6]. The reactions of the scientific community to the desiccated deep-basin model were also divergent. Favourable commentaries were not rare. On the other hand, many critiques were sceptical, or downright hostile.

The importance of clarifying the question of the Messinian salinity crisis did not escape the attention of the JOIDES organisations. A second cruise to the Mediterranean took place in 1975. We are glad to report that we reached a near-concensus on the previously controversial question of the origin of the Mediterranean Evaporite. This article is not a perfunctory report requiring a co-authorship by the shipboard scientific staff. It is a unanimous opinion written by the senior author for ten co-authors, who represent all but two of the shipboard scientific staff during the Leg 42A cruise.

The Miocene Mediterranean

Whereas there seemed to be general agreement that the Messinian (Late Miocene) evaporites were deposited in shallow water conditions, controversy revolved around the basin depths at times of evaporite deposition[7]. The crux of the matter is the genesis of the Mediterranean basins. When did the Mediterranean basins form? In the Early and Middle Miocene before the Messinian salinity crisis?[8] In the Pliocene shortly after the salinity crisis[9]? Or "did the main phase of subsidence occur rather abruptly during the Pleistocene and Holocene"[10]. Syntheses of regional tectonic data led to the conclusion that the deep basins of the Mediterranean have evolved to a stage quite similar to their present configuration before the Late Miocene when the salinity crisis began[4,11–14]. Of the five major Mediterranean basins, the Levantine and Ionian basins may be relic Tethys of Mesozoic age; The Balearic and Tyrrhenian were formed during the Early and Middle Miocene, after the culmination of the Alpine orogeny. Perhaps only the Aegean has undergone significant Plio-Quaternary subsidence.

Deep-sea drilling during the Leg 42A has unearthed convincing evidence that deep Mediterranean basins were in existence before the Messinian. Drilling at Site 372 (Fig. 1) indicated that the Balearic Basin was formed by rifting during the latest Oligocene or earliest Miocene time. Palaeobathymetric analyses on the basis of benthonic foraminifera estimated that this part of the Balearic margin was at least 900 m deep during the Early Miocene (Burdigalian) time. The water depth reached in excess of 1,200 m during the late Burdigalian and subsided gradually to a depth more than 1,500 m before the Middle Miocene ended[15].

The pre-Messinian sequence at Site 372 is mainly hemipelagic, similar to the sediments deposited there today. The planktic and benthic faunas and floras are fully open marine. Aside from benthic foraminifera, psychrospheric ostracods also occur in some Early and Middle

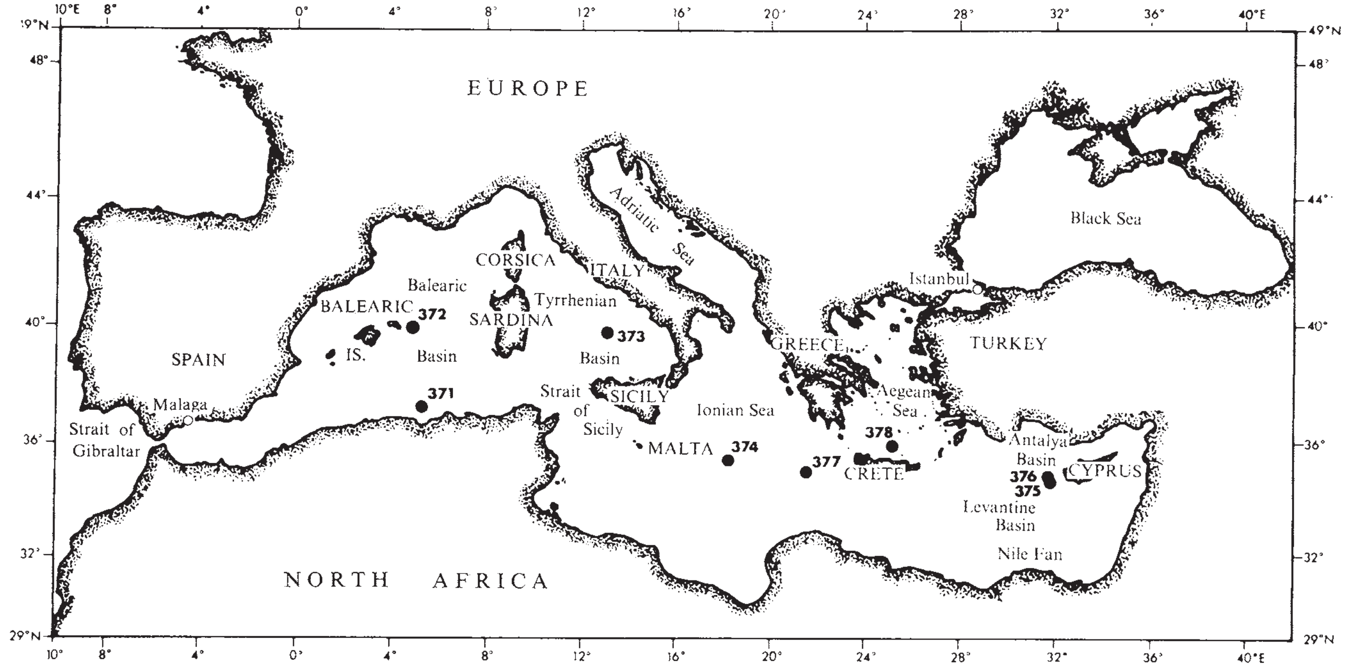


Fig. 1 Drill sites of DSDP Leg 42A.

Miocene cores, indicating water-depths in excess of 1000 m (ref. 16).

Drilling resutls at Site 373 seamount indicated that a deep Tyrrhenian Basin was also in existence during the Messinian. Palaeotemperature estimated for the submarine cementation (by calcite) of the early Pliocene pillow breccias at this site is estimated by isotopic evidence to be 6–8 °C (ref. 17). Such a low temperature implies that the volcanic seamount was deeply submerged then, only a short time after the salinity crisis.

We penetrated beyond the Messinian at Site 375 west of Cyprus in the Levantine Basin. As in Hole 372, the pre-Messinian sequence at this eastern Mediterranean site is also mainly hemipelagic. Palaeobathymetric analyses indicate that the Levantine Sea was a deep, open sea during the Miocene before the Messinian salinity crisis[15].

Events leading to the salinity crisis

Geological reconstructions indicate the presence of an equatorial ocean, which separated Europe from Africa during the Jurassic and Cretaceous and the ocean was named Tethys[14,18]. The connection between the Atlantic and the Indo-Pacific was maintained through a shallow seaway after the joining of the two continents in late Cretaceous[19]. This shelf sea started to disappear during the Burdigalian (late Early Miocene). This was one of the major palaeobiogeographical events of the Tertiary; it was during this period that "the present pattern of land and sea was established"[20]. The joining of Europe and Asia permitted the exchange of land fauna between those continents, and started the differentiation of the Indo-Pacific and Atlantic–Mediterranean marine faunas. Whereas the evidence from vertebrate palaeontology indicates the establishment of first intercontinental connection between Eurasia and Africa during the Burdigalian[21], the micropalaeontological data suggest that there might have been repeated transgression into the Mediterranean from the Indo-Pacific till Middle Miocene time[22] (Fig. 2).

The orogenic movements which fused Eurasia and Africa also raised new mountains in the Taurides, the Hellenides, the Dinarides, and eventually, somewhat later in the Middle or early Late Miocene, the Helvetic Alps. This series of movements led to a separation of the Mediterranean and an eastern European inland sea, the Paratethys. Stratigraphical and palaeobiogeographical data indicate that the Burdigalian connection between the two seas went through the Peri-alpine Depression north of the Alps[22,23]. This seaway was eliminated early in Middle Miocene, when the Alps rose and marine waters withdrew from the Molasse trough. A last thread of contact was probably maintained between the Mediterranean (Langhian) and the Paratethys (early Badenian) through an opening in northern Italy and north-western Yugoslavia. The complete separation of the two inland seas took place some 14 to 15 million years ago during the Serravallian (late Middle Miocene). The last Indo-Pacific flooding that invaded the Paratethys later in the Serravallian (14–13 Myr) did not reach the Mediterranean[22].

The Middle Miocene separation had two consequences. The Paratethys could no longer receive marine water from the Mediterranean nor could the Mediterranean receive freshwaters from that part of Eurasian rivers which now emptied themselves into the Paratethys. When the connection was open, surplus ions resulted from evaporative excess in the Mediterranean may have found their way to the Paratethys, and were deposited as the lower Middle Miocene salts of the Pannonian and Transylvanian Basins[22]. After the loss of communication the Mediterraean was deprived not only of much freshwater influx but also of one of its means of the elimination of evaporative waste.

The Mediterranean's last links to the world ocean were the Betic and the Rif Straits. The deep Betic Strait shoaled after the end of the Middle Miocene; no Late Miocene psychrospheric ostracodes were found inside the Mediterranean[16]. Yet open marine conditions prevailed in the Mediterranean during the earlier parts of the Late Miocene (Tortonian and early Messinian)[24].

The Messinian change from normal marine to an evaporite-forming condition was a sudden event. The palaeobotanical record gives no evidence of an abrupt change in climate. There had been a general trend towards a drier and cooler climate since the Burdigalian, when the Mediterranean was first cut off from the Indian Ocean[25]. Thus we cannot interpret the change from normal marine to evaporative conditions as a response to climatic factors; the change had to be related to a final closure of the openings at the west during the latest Miocene. With the isolation and a serious hydrographic deficit, the salinity crisis of the Mediterranean finally became inescapable.

The Messinian salinity crisis

Seismic records suggested a twofold division of the Mediterranean Evaporite[26]. (1) An Upper Evaporite sequence, with numerous reflectors, up to several hundred metres thick, and consisting of dolomite, gypsum, anhydrite, and some salts. (2) The Main Salt and Lower Evaporite sequence, seismically homogenous salt, up to a thousand metres thick or more, underlain by several evaporite reflectors. The distribution of the Main Salt unit is restricted to the more central part of each of the Mediterranean basins. The distribution of the Upper Evaporite unit is, however, more extensive.

Since drill cores only yielded information on the Upper Evaporite, we depend on land sections for an overview of the Messinian salinity crisis. The onset of the salinity crisis as in Sicily, for example, indicated by the contact of *Calcare di base* on 'Tripoli', signifies a very rapid change from a bathyal environment of hemipelagic sedimentation to a shallow, or subaerial environment of carbonate deposition and diagenesis[24].

The history of the early evaporite deposition can be deciphered from a reference to the section of the Cattolica basin, Sicily[27]. The Lower Evaporite sequence there lies above the Tripoli Formation and includes (1) *Calcare di base*, (2) Cattolica Gypsum, (3) Clastic Gypsum beds, (4) halite and potash salts.

The salts are in general 300–500 m thick. Decima[28] divided a 330-m section of salts at Porto Empedocle into four units. The Unit A is a halite with laminae of anhydrite and is 108 m thick. The bromine content of the halite is about 400 p.p.m. The Unit B is well laminated halite, kainite, polyhalite and anhydrite, and is 115 m thick. The bromine content ranges from 200 to 250 p.p.m. except for the uppermost pure halite which contains some 100 p.p.m. Br. The Units C and D overlie the lower salts unconformably. They are 107 m thick and consist of halite, with anhydrite and anhydritic shales. The halite in these upper units has only traces of bromine (10 p.p.m. or less).

The lower salts with their high Br were precipitated from brines derived from evaporated seawater. In contrast the upper salts were recycled. Sedimentological studies[29] indicated that the upper salts were deposited in shallow saline environments. On the other hand, the well laminated Unit B, with sequences of cyclic lamination that can be correlated for long distances, were precipitated in a relatively deep subaqueous environment.

The Lower Evaporite is overlain uncomformably by a Upper Evaporite of gypsum and marls. A comparison of the submarine Messinian with the Sicily section suggests a similar two-stage evolution of the Messinian salinity crisis in other Mediterranean basins. After an initial desiccation or partial desiccation, the Lower Evaporite was probably precipitated when the supply of brines was sufficiently continuous, to cause the accumulation of thick halite and potash salt deposits on the deepest floor of the Mediterranean basins. Toward the end of the Main Halite deposition, the supply of brine probably ceased because of a complete isolation from the Atlantic. The brine level was drastically drawn down because of evaporative loss. Large areas on the periphery of the salt basins were exposed. Waters from the continent or from local precipitation formed salt creeks, eroding primary salts (for example Units A and B, Porto Empedocle), and depositing secondary salts (for example Units C and D) in the centre of the salt basins. This desiccation period was represented by the widespread unconformity separating the Lower and the Upper Evaporite units. Rivers cut canyons on the margins of the continents and some of these canyons were eventually floored by the Upper Evaporite deposits[26].

The erosional event was ended by a new inundation of the Mediterranean, when the Mediterranean was probably again filled to the brim. The lower marine marls of Messinian age at DSDP Site 372 (Core 9/2) are the first sediments above the unconformity and they may have been deposited during this intra-Messinian flooding. The subsequent history of the Upper Evaporite sedimentation was probably characterised by periodic influx of marine waters into a largely desiccated deep basin[30]. A repetition of marine inundation, followed by isolation, and evaporative draw-down led to the accumulation of marls, stromatolitic carbonates, gypsum, anhydrite and salts, in cyclic sequences.

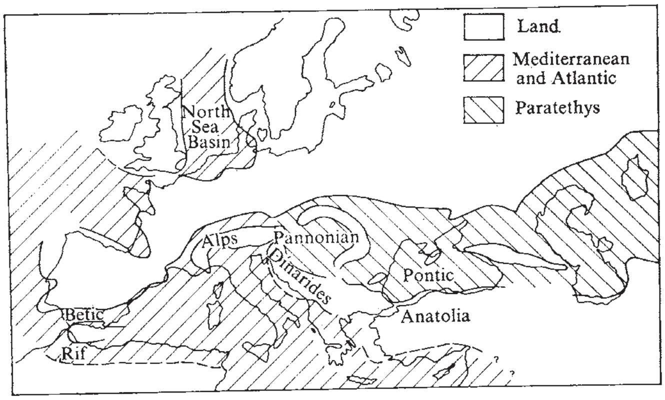
Lago Mare

The geological record of the eastern Mediterranean holes revealed a drastic change in depositional environment during the latest Messinian time before the final Pliocene marine inundation. After the last salt deposition of the Upper Evaporite, the Ionian and Antalya basins were almost totally dried up. Slight changes in the water-budget led to conditions of cyclic sedimentation. The very last Messinian sediments at Sites 374 and 376 are marls, however, deposited in a standing body of water. Isotopic evidence suggests a considerable influx of continental waters to those previously desiccated basins[31].

Site 376 samples contain an *Ammonia–Cyprideis* fauna, indicative of the euryhaline environment. Similar *Cyprideis* and other euryhaline faunas are present in numerous uppermost Messinian sections on land in both the eastern and western Mediterranean countries. The Mediterranean hosted a series of fresh or brackish water lakes toward the end of the Messinian. We propose that the term *Lago Mare* be used to designate the latest Messinian lake (or oligohaline) environments in the Mediterranean, subsequent to the evaporite-deposition, but before the Pliocene marine sedimentation[24].

The change from salt-precipitation in shallow salinas to deposition of marls in *Lago Mare* occurred within a very short time interval probably in less than 100,000 yr. The change implies a radical alteration of the hydrographic budget. There was, however, no drastic climatic change during the Messinian. The environmental change must have been related to a reorganisation of the drainage system in Europe. The sudden appearance of so much fresh or brackish water, together with a typical Paratethyan fauna, probably indicates a sudden inundation of the desiccated Mediterranean by Paratethyan waters from eastern Europe (Fig. 3).

Fig. 2 Middle Miocene (16–18 Myr) Palaeogeography.



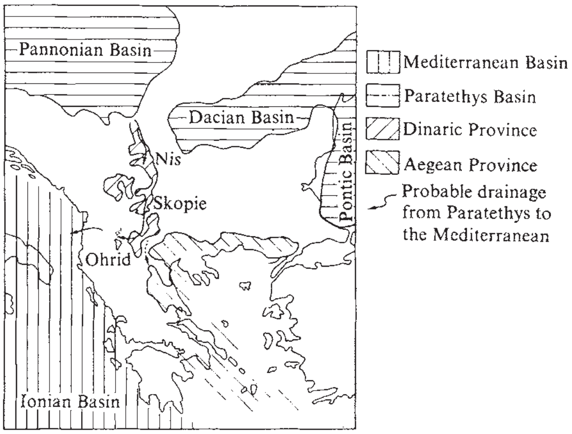


Fig. 3 Late Miocene (5.5 Myr) Palaeogeography.

That such an invasion did take place has been speculated by biogeographers on the basis of the occurrence of relic Paratethys faunas (including freshwater fish, molluscs and birds) in isolated areas of circum-Mediterranean land today[32]. The evidence from Paratethys also indicated that it suddenly lost much of its waters to the Mediterranean in late Neogene[33]. In fact, the drainage reorganisation at this time is believed to have resulted in an evaporative excess of the hydrographic budget of the Black Sea, leading to a partial desiccation of that deep Paratethyan basin[34].

The *Lago Mare* may have occasionally extended to the western Mediterranean. The *Cyprideis* fauna is present in land sections in Algeria, Spain, Tuscany, and in Sicily[24]. A brackish water sediment is present in the Balearic Hole 124 within the evaporite sequence and may be equivalent to the lower part of the *Lago Mare* sequence of the eastern Mediterranean. The very last Messinian sediments there below the Pliocene are, however, restricted marine deposits. It seems that towards the end of the Messinian the marine waters spilled over the western basins before they reached the east. The restricted marine facies of the uppermost Messinian in the Balearic and Tyrrhenian Basins are probably time equivalent in part to the upper *Lago Mare* deposits of the Ionian and Levantine Basins. The latter were inundated after the seawater spilled over Sicilian Channel. The early Pliocene (Trubi) inundation probably did not reach the Red Sea which was separated from the Mediterranean by the Isthmus of Suez. The marine invasion there was dated as occurring some 3.5–4 Myr ago, when a connection to the Indian Ocean was established through the Strait of Bab el Mandeb[35].

Pliocene flooding and Plio-Quaternary subsidence

Leg 42A drilling confirmed the Leg 13 drilling results that the first Pliocene sediments above the Messinian are deep and open marine hemipelagic sediments. The Messinian salinity crisis was ended by the Pliocene flooding.

Palaeobathymetric analyses indicated that the Pliocene sediments immediately above the Mio-Pliocene contact are in excess of 1,000 m, or 1,500 m in depth. The drilling evidence proved that deep Mediterranean depressions which had existed before the Messinian salinity crisis were still there at the end of the crisis. Seismic evidence indicates considerable Plio-Quaternary subsidence[36]. The subsidence is in part induced by the isostatic load of the water flooding the basins[4]. Additional subsidence could be related to cooling of the mantle under the basins, or to continued tectonic activities which may have deepened the Mediterranean back-arc basins[26]. There have been considerable Plio-Quaternary tectonic activities in the circum-Mediterranean regions. The evaporite basins of Sicily, Calabria, Apennines, Tellian Atlas, Ionian Islands, Crete, Cyprus, and so on, were uplifted and emerged. Meanwhile continental margins locally (Nile and Rhone deltas, Israeli shelf, and so on) underwent subsidence[37]. Those activities have modified the post-Messinian palaeogeography. The fact remains, however, that the Mediterranean basins owed their genesis to earlier movements, even though their floor may have been uplifted or subsided somewhat during the last five million years.

Impact of the Mediterranean salinity crisis

The desiccation of the Mediterranean took place 5.5 Myr ago. Such a geologically recent catastrophic event left behind not only a giant evaporite deposit, it also had a great impact on the modern world, on the circum-Mediterranean landscape, on regional and global climates, and on the evolution and distribution of plants and animals.

The lowering of the base-level of erosion led to the deep incision of rivers which drained into the Mediterranean[4]; even the southern Alpine lakes may have been Messinian canyons modified by Pleistocene glacial erosion[38]. The exposure of Mediterranean bottom promoted an unusually active Late Miocene groundwater movement, which was probably responsible for the initiation of karst topography in Yugoslavia and in other Mediterranean countries. The uneven topography of the Mediterranean Ridge may have been a modified karst-development[4], anomalous drilling behaviour noted during Leg 42A drilling on the Ridge suggests presence of submarine caverns.

The salinity crisis induced a continued change towards a cooler and more arid climate in the circum-Mediterranean. The Antarctic ice sheet expanded greatly during the Messinian[39], and the Arctic ice sheets may have begun to form then[40].

Biologists are only beginning to explore the implications of the Miocene Mediterranean desiccation. The present Mediterranean fauna is similar to that of the Pliocene, but very different from that of the Miocene, a fact noted by Lyell more than 100 yr ago when he first established the Miocene and Pliocene Epochs. The periodic conversion of an inland sea into dry land also permitted a migration of land animals; numerous examples of exchanges between Africa and Europe during the Messinian have been found[41,42]. With the sudden Pliocene flooding, animals stranded on the Mediterranean islands would become isolated and develop endemism[41,42]. Other usual aspects of the present Mediterranean land faunas may also be related to the unusual Messinian event. We might ask, for example, if the unusual habit of the circum-Mediterranean eels to breed in the Mediterranean, rather than in the Sargasso Sea, might be traced back to the time when the gate to the Atlantic was closed. We might also invoke the Messinian *Lago Mare* expansion to explain the similarity of relic freshwater faunas in France, Spain, and North Africa to those of the present Caspian. The impact of the Messinian salinity crisis and the accompanying climatic changes must have greatly influenced the distribution of land plants. The aridity led to temporary or permanent expansion of savanna vegetations. The impact on plant-evolution is subtle, but intriguing. It was suggested that some of the Mediterranean floras (for example *Medicago*) evolved from perennial to annual forms so as to endure longer period of severe drought, and from cross- into self-pollinators because insects could not have followed the new hardy plants into the hot dry environment (K. Lesins, personal communication).

We close this article in a contemplative mood. Biochemical studies suggest that the African ape–human divergence took place 5 or 6 Myr ago during the Messinian[43,44], just about the time when what is known to be the earliest hominid lived in Kenya[45]. Is the timing purely coincidental, or did the great expansion of the East Africa savannas at the time of the Mediterranean salinity crisis promote hominid evolution? Is our very being today traced back to that unusual event?

Received 27 January; accepted 1 April 1977.

[1] Hsü, K. J., Ryan, W. B. F. & Cita, M.B. *Nature* **242,** 240 (1973).
[2] Hsü, K. J. *Earth Sci. Rev.* **8,** 371 (1972).
[3] Sylvester-Bradley, P. C. *Geol. Mag.* **110,** 73 (1973).
[4] Hsü, K. J., Cita, M. B. & Ryan, W. B. F. *I.C.R. DSDP* (*Initial Reports of the Deep Sea Drilling Project*, U.S. Government Printing Office, Washington DC) **13,** 1023 (1972).
[5] Nesteroff, W. D. *ICR DSDP* **13,** 673 (1972).
[6] Wezel, F. C. *Giornale di Geologia* **39,** 447 (1974).
[7] Drooger, C. W. in *Messinian Events in the Mediterranean* (ed. Drooger, C. W.), 263 (North-Holland, Amsterdam, 1973).
[8] Argand, E. *XIIIe Congr. geol. intern. Bruxelles*, CR 171 (1924).
[9] Selli, R. & Fabbri, M. *R.C. Accad. Lincei* **8,** 104 (1971).
[10] Neev, D., Almagor, G., Arad, A., Ginsburg, A. & Hall, J. K. *Geol. Surv. Israel, Bull.* **68,** 1 (1976).
[11] Smith, A. G. *Geol. Soc. Am. Bull.* **82,** 2039 (1971).
[12] Dewey, J. F., Pittman, W. C., Ryan, W. B. F. & Bonin, J. *Geol. Soc. Am. Bull.* **84,** 3137 (1973).
[13] Biju-Duval, B., Dercourt, J. & Le Pichon, X. *Recherche* **7,** 811 (1976).
[14] Hsü, K. J. & Bernoulli, D. *ICR DSDP* **42A** (in the press).
[15] Wright, R. *ICR DSDP* **42A,** (in the press).
[16] Benson, R. H. *ICR DSDP* **42A,** (in the press).
[17] Bernoulli, D., Garrison, R. E. & McKenzie, J. A. *ICR DSDP* **42A** (in the press).
[18] Suess, E. *Nat. Sci.* **2,** 180 (1893).
[19] Hallam, T. in *Palaeontological Ass. spec. Publ.* **12** (ed. Hughes, N. F.) (1973).
[20] Adams, C. G. in *Atlas of Paleobiogeography* (ed. Hallam, A.) 453 (Elsevier, Amsterdam, 1973).
[21] Savage, R. J. G. *Systematics Ass. Publ.* **7,** 247 (1967).
[22] Rögl, F., Steiniger, F. & Müller, C. *ICR DSDP* **42A** (in the press).
[23] Gignoux, M. *Geologie Stratigraphique*, 4th edn (Masson & Cie, Paris, 1950).
[24] Cita, M. B., Wright, R., Ryan, W. B. F., & Longinelli, A. *ICR DSDP* **42A** (in the press).
[25] Benda, L. in *Messinian Events in the Mediterranean* (ed. Drooger, C. W.), 256 (North-Holland, Amsterdam, 1973).
[26] Montadert, L. C., Letouzey, J. & Mauffret, A. *ICR DSDP* **42A** (in the press).
[27] Decima, A. & Wezel, F. C. *ICR DSDP* **13,** 1234 (1972).
[28] Decima, A. *Proc. Messinian Seminar, Erice, Sicily* (1975).
[29] Schreiber, B. C., Friedman, G. M., Decima, A. & Schreiber, E. *Sedimentology* **23** (1976).
[30] Garrison, R. E. *et al. ICR DSDP* **42A** (in the press).
[31] McKenzie, J. A. & Ricchiuto, T. E. *ICR DSDP* **42A** (in the press).
[32] Stankovic, S. *The Balkan Lake Ohrid and its Living World Mongraphiae Biologicae* **9** (W. Junk, The Hague, 1960).
[33] Jiricek, R. *VIth Congr. Med Neogene Stratigraphy, Bratislava*, 33 (1975).
[34] Hsü, K. J. *ICR DSDP* **42B** (in the press).
[35] Hsü, K. J., Stoffers, P. & Ross, D. A. *Abstr. 25th Int. Geol. Congr. Sydney*, 894 (1976).
[36] Morelli, C. *Bull. de l'étude en commun de la Méditerranée* **7,** 29 (1975).
[37] Ryan, W. B. F. *Sedimentology* **23,** 791 (1977).
[38] Finckh, P. *Messinian Seminar* **2** (Gargnano, Italy, 1976).
[39] Hayes, D. E. *et al. ICR DSDP* **28** (1975).
[40] Van Hinte, J. *ICR DSDP* **38** (1976).
[41] Hsü, K. J. *Naturwissenschaften* **61,** 137 (1974).
[42] Azzaroli, A. & Guazzoni, G. *Messinian Seminar* **2,** 60 (1976).
[43] Sarich, V. M. & Wilson, A. C. *Science* **158,** 1200 (1967).
[44] Goodman, M. *et al. Aeromedical Res. Lab.* ARL-TR-69-10 (Holloman A. F. B., 1969).
[45] Ardrey, R. *The Hunting Hypothesis* 47 (Collins, London, 1976).

Catastrophic chemical events in the history of the ocean

William T. Holser

Max-Planck-Institut für Chemie, D-6500 Mainz, Germany (BRD)
Department of Geology, University of Oregon, Eugene, Oregon 97403

Catastrophic chemical events are characterised by sharp rises in $\delta^{34}S$ in the surface of the whole world ocean, and by greater overshoots locally. Three events are recognised and named for the formation in which they are most sharply displayed. The sharpness of the rise in $\delta^{34}S$ suggests that the sulphide deposition necessary to explain it must have been accumulating residual high-$\delta^{34}S$ seawater for some tens of millions of years out of contact with the surface ocean. A modified geological model is presented: brine generated by evaporite deposition is stored in deeps of a mediterranean basin; underneath the brine, pyrite precipitation builds a store of brine heavy in $\delta^{34}S_{SO_4}$, whose corresponding buildup of $\delta^{38}O_{SO_4}$ may balance the decrease of $\delta^{38}O_{SO_4}$ from evaporite deposition. Catastrophic mixing of the brine and the surface ocean, initiated by destruction of the storing basin, is the source of the sharp rise in the sulphur isotope age curve detected world-wide in evaporites. These events have important implications not only for modelling of the chemical history of the ocean, atmosphere, and sediments, but also for the explanation of faunal crises, and the many aspects of geology that depend on the composition and circulation of the oceans and their peripheral basins.

IT has been known for some time that the sulphur isotope ratio in the world ocean surface has undergone major excursions during the period (Proterozoic–Phanerozoic) that could be documented from evaporite sulphate samples[1–3]. The resulting sulphur isotope age curve has recently been updated with many new analyses of sulphur isotopes[4,5], supplemented by measurements of oxygen isotopes from some of the same sulphates[5,6]. The interpretations of these isotope age curves have focused mainly on explaining the trends of $\delta^{34}S$ as a result of widespread variations in biological reduction of sulphur into shales; on subsequent oxidative erosion into the sea; and with possible coupling of the carbon cycle to maintain atmospheric oxygen (refs 3, 5, 7–12). My purpose here is to discuss some more dramatic but less well-documented features of the isotope age curves, and to discuss whether they record catastophic chemical events that are specific in time and place.

Upward jumps in $\delta^{34}S$

Fig. 1 shows as a solid line the mean best estimate for $\delta^{34}S$ in sulphate evaporite minerals in equilibrium with the surface of the world ocean[4,5]. In constructing this curve greater weight was attributed to values whose world-wide distribution bore out their origin in the ocean surface as a whole, and less weight to results that were found in a narrow range of time and place. But it is worth noting that those of the latter deviations that are not so widespread may have considerable significance.

Marks on Fig. 1 highlight three rises in $\delta^{34}S$; and a solid line in Fig. 2 repeats these parts of the curve on an enlarged scale. These rises are so large and take place over such a short time, that I have labelled them chemical events by analogy with the nomenclature of magnetic reversals. Table 1 lists some characteristics of these three events. There are differences that may be significant, but some common features are: (1) The mean curve established by world-wide evaporite sampling rises sharply. (2) The rise is highly accentuated by a positive overshoot, in one formation in one basin, which gives its name to the event. The overshoot peak is a step function within the limits of stratigraphic control. (3) It is difficult to fix the absolute time interval within which the event is bracketed. Each seems to have taken place within one stratigraphic stage, probably much less than 5 Myr. (The times given in Table 1 are only scaled by inter-